

## First Hyperpolarizabilities of Hexaazatriphenylene Derivatives: Octupolar Nonlinear Optical Molecules

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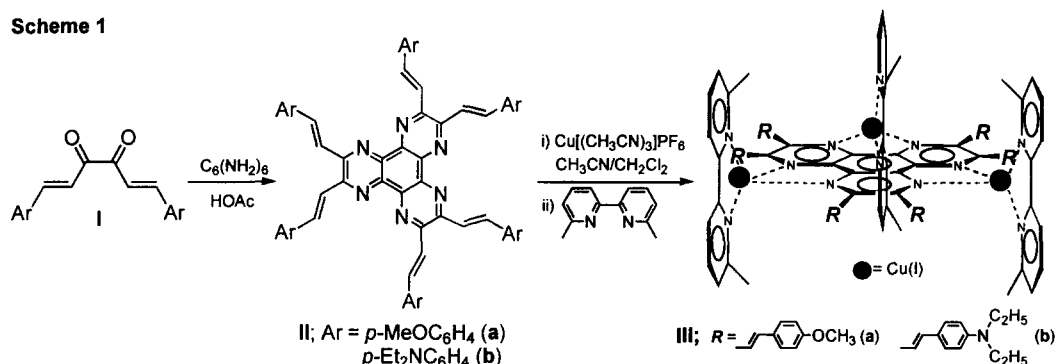
**Abstract:** The first evaluation of the  $\beta$  values and thermal stability for octupolar molecules derived from hexaazatriphenylene derivatives is reported. © 1998 Elsevier Science Ltd. All rights reserved.

Octupolar molecules with  $C_3$  symmetry have been shown to exhibit first hyperpolarizability comparable to those for the donor-acceptor dipoles.<sup>1</sup> Also there has been a theoretical report that the  $\beta$  value of the octupolar molecules increases monotonously as the charge transfer character of the electronic ground state increases, unlike donor-acceptor dipole-type organic molecules which show the maximum value of  $\beta$  at the optimized charge transfer character of the ground state.<sup>2</sup> However, little experimental studies have been conducted to establish the structure-property relationship of the octupolar molecules.

One of the promising candidates for the octupolar NLO chromophore is a hexaazatriphenylene (HAT) derivative. HAT and the hexaphenyl derivatives are planar compounds with three metal coordinating sites.<sup>3</sup> Introduction of the *p*-methoxy- or *p*-dialkylaminostyryl groups at the 2,3,6,7,10,11-positions of HAT would produce an octupolar molecule, in which the three donor-acceptor dipoles are arranged with  $C_3$  symmetry. These compounds are expected to exhibit significant first-order hyperpolarizability since the donors and electron-accepting hexaaza groups are connected by the conjugated  $\pi$ -system, which can serve as a bridge for the mobile electrons. Furthermore, the  $\beta$  values of these compounds can easily be optimized by changing the donor and acceptor strength, either by substituting a different electron-donating group at the *para* positions of the styryl moieties or by coordinating the hexaaza groups with metal ions.<sup>3</sup> Finally, it could provide a building block for a NLO supramolecule with ideal arrangement of the octupolar molecules in the solid state when coordinated with a linear oligobipyridine ligand.<sup>4</sup> Here, we report the first result of the structure-property studies for a series of 2,3,6,7,10,11-hexastyryl-1,4,5,8,9,12-hexaazatriphenylene derivatives.

Table 1 lists the HAT derivatives that we have synthesized. The general methodology for the synthesis of these compounds is shown in Scheme 1. Compound **I** was synthesized by the modified procedure of the

Scheme 1



literature method.<sup>5</sup> The yield was improved significantly by employing a high dilution method. Compound **II** was prepared by reacting **I** with hexaaminobenzene.<sup>3,7</sup> Complexation of **II** with Cu[(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> followed by the ligand exchange with 5,5'-dimethylbipyridine afforded **III** in reasonable yields.<sup>8</sup> The spectral data and the results of elemental analysis for all of the products as well as the FAB-mass data for **III** were consistent with the proposed structures. The second-order nonlinear hyperpolarizability of these compounds were determined in DMSO by hyper-Rayleigh scattering as reported previously.<sup>9,10</sup> The fundamental wavelength was shifted to 1560 nm by using a Raman shifter containing deuterium in order to avoid the absorption of the HRS signal by the chromophores.

The linear and nonlinear optical properties and thermal stability of various chromophores are summarized in Table 1. The  $\lambda_{\text{max}}$  values are shifted to a longer wavelength as the donor strength is increased. Similar red shift is observed as the acceptor is made more electron withdrawing by the complexation of the 1,10-phenanthroline moiety with Cu(I). All of the chromophores showed  $\lambda_{\text{cut off}} < 700$  nm and emitted little fluorescence when excited at the  $\lambda_{\text{max}}$ . This result indicates the reliability of the HRS measurement, as it is neither underestimated by the absorption bands nor overestimated by the fluorescence.<sup>10</sup>

Table 1. Optical properties and thermal stability of hexaazatriphenylene (HAT) derivatives

Compound	$\lambda_{\text{max}}/\text{nm}$ (log $\epsilon$ ) <sup>a</sup>	$\beta$ , 10 <sup>-30</sup> esu <sup>a</sup>	$\beta(0)$ , 10 <sup>-30</sup> esu <sup>b</sup>	Td/°C <sup>c</sup>
<b>IIa</b>	460 (4.49)	18	11	360
<b>IIb</b>	526 (4.90)	50	29	343
<b>IIIa</b>	468 (4.90)	31	18	327
<b>IIIb</b>	532 (4.55)	197	93	346

<sup>a</sup>Solvent was DMSO. <sup>b</sup>Corrected at  $\lambda_0 \rightarrow \infty$  by using the two level model.<sup>11</sup> <sup>c</sup>Determined by thermal gravimetric analysis (TGA).

For all compounds, the  $\beta$  values are larger when the *para* styryl substituent is made more electron-donating, i.e., **IIb** > **IIa** and **IIIb** > **IIIa**. The  $\beta$  values increase as the acceptor strength is increased by the complexation of the HAT with Cu(I) at the center of the octupolar molecules, i.e., **IIIa** > **IIa** and **IIIb** > **IIb**. These results are consistent with the theoretical prediction that the  $\beta$  value should increase as the donor and acceptor strength is increased.<sup>2</sup> It is interesting to note that the  $\beta$  values for the Cu(I) complexes **III** increase more steeply than the parent HAT derivatives, **IIa** and **IIb**, by the stronger electron-donating substituent. Finally, the experimental decomposition temperatures are all above 320 °C probably due to their planar structures.

In conclusion, we have synthesized a series of hexaazatriphenylene (HAT) derivatives and measured their  $\beta$  values and thermal stability. They exhibit appreciable  $\beta$  values and high thermal stability. The  $\beta$  value increases as the donor and acceptor strength is increased.

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5. **Ia** was synthesized by the literature procedure except that butane-2,3-dione (2.0 g, 20 mmol) in 100 mL methanol was added to a solution containing *p*-anisaldehyde (7.3 g, 50 mmol) and piperidine (1.3 mL) in 20 mL of methanol with a microsyringe for 6 hrs at the reflux temperature.<sup>6</sup> The solution was cooled to room temperature and stored in a refrigerator until yellow precipitates were produced. The product was recrystallized from ethanol. Yield, 2.2 g (34 %), M.p. 167 °C (lit<sup>6</sup> mp 167 °C).
6. **Ib** was synthesized by the same procedure from *p*-diethylaminobenzaldehyde (9.5 g, 54 mmol). Yield, 3.5 g (32 %); M.p. 182-184 °C; IR (KBr): 2972, 1560, 1517 cm<sup>-1</sup>; <sup>1</sup>NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.1 (t, *J* = 4.9, 12H), 3.4 (q, *J* = 4.7, 8H), 6.6 (d, *J* = 6.0, 4H), 7.1 (d, *J* = 10.8, 2H), 7.4 (d, *J* = 5.8, 4H), 7.8 (d, *J* = 10.8, 2H). Anal calcd for C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.19; H, 7.97; N, 6.92. Found: C, 77.18; H, 8.08; N, 6.95.
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7. **IIa** was synthesized by adding hexaaminobenzene (0.18 g, 1.1 mmol) in 10 mL H<sub>2</sub>O to **Ia** (1.0 g, 3.1 mmol) in 60 mL THF/10 mL HOAc. The solution was stirred for 6 hrs at room temperature and stored in a refrigerator until deep red solid was precipitated. The solvent was evaporated and the solid product was purified by chromatography on a silica gel column. The mixture was eluted with hexane/ethyl

acetate (8/1) until all of the reactants were removed and then with ethyl acetate to obtain the pure product. Yield, 0.9 g (80 %); M.p. 286 °C; IR (KBr): 1598, 1511  $\text{cm}^{-1}$ ;  $^1\text{NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.8 (s, 18H), 6.9 (d,  $J = 8.7$ , 12H), 7.4 (d,  $J = 15.0$ , 6H), 7.5 (d,  $J = 9.0$ , 12H), 8.2 (d,  $J = 14.7$ , 6H). Anal calcd for  $\text{C}_{66}\text{H}_{54}\text{N}_6\text{O}_6$ : C, 77.17; H, 5.30; N, 8.18. Found: C, 77.05; H, 5.28; N, 8.47.

**IIb** was synthesized by the same procedure as above except that **Ib** (2.0 g, 5.0 mmol) in 120 mL THF-20 mL HOAc and hexaaminobenzene (0.25 g, 1.5 mmol) in 20 mL of  $\text{H}_2\text{O}$  were used as the reactants, and the reaction temperature was elevated to 60 °C. The product was purified by a column chromatography on a silica gel column by using 3 % MeOH/ $\text{CHCl}_3$  as an eluent. Yield 1.1 g (60 %); M.p. 343 °C (dec); IR (KBr): 2922, 1569  $\text{cm}^{-1}$ ;  $^1\text{NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.2 (t,  $J = 6.9$ , 36H), 3.4 (q,  $J = 6.6$ , 24H), 6.8 (d,  $J = 9.0$ , 12H), 7.6 (d,  $J = 15.6$ , 6H), 7.7 (d,  $J = 8.7$ , 12H), 8.4 (d,  $J = 15.3$ , 6H). Anal calcd for  $\text{C}_{84}\text{H}_{96}\text{N}_{12}$ : C, 79.20; H, 7.60; N, 13.19. Found: C, 79.47; H, 7.61; N, 13.36.

8.  $[\text{Cu}(\text{I})\text{HAT}(\text{bipy})_3]$  complexes **III** were prepared by the following procedure. A solution of  $[\text{Cu}(\text{I})(\text{CH}_3\text{CN})_3\text{PF}_6]$  (1.1 g, 2.9 mmol) in 5.0 mL  $\text{CH}_3\text{CN}$  was added to the solution containing **IIa** (1.0 g, 0.98 mmol) in 20 mL  $\text{CH}_2\text{Cl}_2$  under argon atmosphere and stirred for 30 min at room temperature. To this solution was added the solution of 6,6'-dimethyl-2,2'-bipyridine (0.54 g, 2.9 mmol) in small amount of  $\text{CH}_2\text{Cl}_2$  and stirred for 3 hrs under argon atmosphere. The solvent was evaporated in vacuo and the solid mixture was washed thoroughly with ethyl acetate until all of the reactants were removed. The product was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and ethyl acetate was added dropwise until green rod-like crystals were obtained. Yield 1.7 g (80%); M.p. 327 °C (dec); IR (KBr): 1600  $\text{cm}^{-1}$ ;  $^1\text{NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.4 (s, 18H), 3.8 (s, 18H), 6.6 (m,  $J = 9.6$ , 24H), 7.1 (d,  $J = 15.8$ , 6H), 7.2 (d,  $J = 7.8$ , 6H), 7.6 (d,  $J = 15.8$ , 6H), 7.6 (m, 12H). Anal calcd for  $\text{C}_{102}\text{H}_{90}\text{F}_{18}\text{N}_{12}\text{O}_6\text{P}_3\text{Cu}_3$ : C, 55.55; N, 7.62; H, 4.11. Found: C, 55.58; N, 7.59; H, 4.05. FAB-mass:  $m/z$  (%): 2060 (62)  $[\text{M}^+ - \text{PF}_6]$ .

**IIIb** was prepared by the same procedure as above except that **IIb** (0.41 g, 3.3 mmol) was used as the reactant. The product was dissolved in a small amount of acetonitrile and ether was added dropwise until the purple crystals were obtained. Yield, 0.48 g (60 %); M.p. 346 °C (dec); IR (KBr): 1587  $\text{cm}^{-1}$ ;  $^1\text{NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.2 (t,  $J = 7.0$ , 36H), 2.4 (s, 18H), 3.4 (q,  $J = 6.8$ , 24H), 6.2 (d,  $J = 9.0$ , 12H), 6.4 (d,  $J = 8.6$ , 12H), 7.0 (d,  $J = 15.4$ , 6H), 7.2 (d,  $J = 6.6$ , 6H), 7.6 (d,  $J = 16.0$ , 6H), 7.8 (m, 12H). Anal calcd for  $\text{C}_{120}\text{H}_{132}\text{F}_{18}\text{N}_{18}\text{P}_3\text{Cu}_3$ : C, 58.78; N, 5.43; H, 10.28. Found: C, 58.29; N, 5.59; H, 10.37. FAB-mass:  $m/z$  (%): 2304 (20)  $[\text{M}^+ - \text{PF}_6]$ .

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